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#### REMARKS

##### General

Claims 1-6 and 8-17 are pending in the application. Claim 7 has been canceled without prejudice. Reconsideration and allowance of pending claims 1-6 and 8-17 of the present application are respectfully requested.

##### The objection to the specification should be withdrawn

The examiner has objected to the specification because of the term "fluorormocers" being an "undefined term." The examiner is referred to the enclosed copy of an article entitled "PERFLOUROARYL SUBSTITUTED INORGANIC-ORGANIC HYBRID MATERIALS" by C. ROSCHER and M. POPALL, printed in Materials Research Society Symposium Proceedings, Vol. 435, 1996, which is before the priority date of the present application. As can be seen from this article, "ORMOCER®" is a registered trademark of the Fraunhofer Gesellschaft in Germany, and is an acronym derived from "organically modified ceramic." Thus, the term "ORMOCER®" was available and known to the person of ordinary skill in the art at the priority date of the present invention. The term "fluorormocers," to which the Examiner objected, is derived from "fluorine" and "ormocers," and the term "fluorormocers" inherently means

"organically modified ceramics containing fluorine." Thus, Applicants respectfully submit that the term "fluorormocers" is not an undefined term but was known to the person of ordinary skill at the priority date of the present invention. In any case, the specification has been amended to explicitly recite this definition. Hence, the objection to the specification should be withdrawn.

**The 35 U.S.C. §112 rejection should be withdrawn**

The examiner has rejected claims 6-8, 11, 13, 15 and 17 under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicants regard as the invention.

Concerning claim 7, the Examiner has stated that the term "fluorormocers" renders claim 7 indefinite because "it is not a commonly used term in the art nor is it defined by the specification." As already pointed out above, the term "fluorormocers" is derived from "fluorine" and "ormocers," both being terms commonly known in the art, as shown in the enclosed article by C. ROSCHER and M. POPALL.

Furthermore, the examiner has rejected claims 6, 7, 8, 11, 13 and 15 as containing improper Markush language. As the examiner shall ascertain, claims 6, 7, 8, 11, 13 and 15 have been amended in accordance with the examiner's suggestions to overcome this rejection. In

addition, the examiner has rejected the term "firmly" in claim 17 as being indefinite. As the Examiner shall ascertain from the amended claims, "firmly" has been deleted in claim 17.

Finally, the examiner has rejected claim 17 because the limitation that the coating "passes a cross hatch test" is allegedly undefined and indefinite. In claim 17, "cross hatch test" has been changed to "cross-cut test." "Cross hatch test" is just another expression for "cross-cut test," which is well known in the art as shown by the enclosed copy of the ISO Standards Handbook, which shows the ISO Standard 2409 from 1992 concerning the cross-cut test. Since the ISO Standards are well within the knowledge of the person of ordinary skill in the art, Applicants respectfully submit that the limitation "cross-cut test" (as well as the limitation "cross hatch test") is clear to the skilled person such that the test can be performed without undue experimentation.

In view of the above, Applicants respectfully submit that claims 6-8, 11, 13, 15 and 17 are in conformance with the requirements of 35 U.S.C. § 112, second paragraph, such that the 35 U.S.C. § 112, second paragraph, rejection should be withdrawn.

The 35 U.S.C. §102 rejection should be withdrawn

The examiner has rejected claims 1, 4-8, 10, 11 and 17 under 35 U.S.C. § 102(b) as being anticipated by the Ellison et al. reference. Furthermore, the examiner has rejected claims 1-3, 6, 11-13 and 17 under 35 U.S.C. § 102(b) as being anticipated by the Gneiss et al. reference. Also, the examiner has rejected claims 1, 4-8, 10, 11 and 14-17 under 35 U.S.C. § 102(b) as being anticipated by the Sugimoto et al. reference. The rejections should be withdrawn for at least the following reasons.

Amended claim 1 relates to an element for use in a motor vehicle, having an anti-adhesive surface coating acting as a protective layer wherein the coating contains at least one compound selected from the group consisting of fluoromocers, fluorine-containing silanes, polymeric fluorocarbon resins, and partially fluorinated polymers.

The Ellison et al. reference states in column 3, lines 28-32 that "[t]he decorative film, as shown in FIG. 2, comprises a substantially molecularly unoriented weatherable cast film 13 which has pigments uniformly distributed therein, and a bonding layer 14 formed of a different polymer adhered to the inner side of the cast film." Column 7, lines 37-38 indicate that the "weatherable cast film" is "formed from an alloy of an acrylic polymer and polyvinylidene fluoride." In addition, according to the examiner, the Gneiss et al. reference teaches an air flow meter comprising a plastic material

coating on one surface of the meter to protect the meter from inaccuracies that can arise from long-term soiling over a period of time wherein a suitable material for the plastic coating is one that is intrinsically resistant to soiling deposits. Furthermore, according to the examiner, the Sugimoto et al. reference teaches an automotive fuel hose and fuel pump diaphragm comprising a laminate of a fluororubber inner layer bonded to an outer layer.

However, as the examiner shall ascertain, none of the Ellison et al. reference, the Gneiss et al. reference and the Sugimoto et al. reference teaches or suggests the coating containing at least one compound selected from the group consisting of fluoromocers, fluorine-containing silanes, polymeric fluorocarbon resins, and partially fluorinated polymers as recited in pending claim 1. Thus, Applicants respectfully submit that claim 1 is in allowable condition. Furthermore, since claim 7 has been canceled without prejudice, the rejection of claim 7 is moot. Similarly, since claims 2-6, 8 and 10-17 ultimately depend from claim 1, claims 2-6, 8 and 10-17 are also allowable by virtue of their dependence on allowable claim 1. Thus, the rejection under 35 U.S.C. § 102(b) of claims 1, 4-8, 10, 11 and 17 as being anticipated by the Ellison et al. reference, the rejection of claims 1-3, 6, 11-13 and 17 as being anticipated by the Gneiss et al. reference, and the rejection of claims 1, 4-8, 10, 11 and 14-17 as being

anticipated by the Sugimoto et al. reference should be withdrawn.

**The 35 U.S.C. §103 rejection should be withdrawn**

The examiner has rejected claim 9 under 35 U.S.C. § 103(a) as being unpatentable over the Ellison et al. reference. While Applicants disagree with the merits of the examiner's contention that the specific element as claimed in claim 9 would have been obvious, it is noted that since claim 9 ultimately depends from claim 1, claim 9 is also allowable by virtue of its dependence on allowable claim 1.

Furthermore, the examiner has rejected claims 4-8 and 10 under 35 U.S.C. § 103(a) as being unpatentable over the Gneiss et al. reference in view of the May reference. Since claim 7 has been canceled without prejudice, the rejection of claim 7 is now moot. While Applicants disagree with the merits of the examiner's contention that the specific element as claimed in claims 4-6, 8 and 10 would have been obvious, it is noted that claims 4-6, 8 and 10 ultimately depend from claim 1, and since the May reference does not remedy the deficiencies of the Gneiss et al. reference as applied against claim 1, claims 4-6, 8 and 10 are also allowable by virtue of their dependence on allowable claim 1.

Therefore, the rejections under 35 U.S.C. § 103(a) should be withdrawn.

## Conclusion

In view of the foregoing, all rejections and objections have been obviated. Allowance of claims 1-6 and 8-17 is respectfully requested.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

The paragraph beginning at p. 4, line 3, has been amended as follows:

A solution of a fluorinated polymer and/or of a fluorormocer, which is organically modified ceramics containing fluorine, in a preferably fluorine-containing solvent is applied using dipping methods, or sprayed, spin-coated, brushed, sprinkled, doctored, rolled, or vapor deposited on as surface coating 20 to sensor element 10. Depending on the application method used and the ratio of solvent to fluorinated polymer, the thickness of surface coating 20 is easily adjustable within the range of about 10 nm to 10  $\mu\text{m}$ .

In the Claims:

Please cancel claim 7 without prejudice.

Please amend claims 1, 6, 8, 11, 13, 15 and 17 as follows:

1. (Amended) An element for use in a motor vehicle, comprising:

an anti-adhesive surface coating acting as a protective layer.



wherein the coating contains at least one compound selected from the group consisting of fluoromocers, fluorine-containing silanes, polymeric fluorocarbon resins, and partially fluorinated polymers.

6. (Amended) The element according to Claim 1, wherein the coating reduces an accumulation, on a surface of the element, of at least one of: dirty water, mineral oil, spray water, silicon oil, soot, salts, hydrocarbons, ~~and~~ or dust particles.

8. (Amended) The element according to Claim 1, wherein the coating is one of a fluorine-containing polymer film ~~and~~ or a fluorosilane coating.

11. (Amended) The element according to Claim 1, wherein the element is composed of at least one of silicon, silicon nitride, silicon dioxide, glass, metal, a polymer ~~and~~ or a ceramic.

13. (Amended) The element according to Claim 2, wherein the sensor element is integrated in one of a humidity sensor, a climatic sensor, an air quality sensor, a temperature sensor ~~and~~ or an airbag sensor.

15. (Amended) The element according to Claim 1, wherein the coating is applied to inner walls of one of: gas-supply channels ~~and~~ or air-supply channels.

17. (Amended) The element according to Claim 1, wherein the coating is ~~firmly~~ adhering and passes a ~~cross-hatch~~ cross-cut test.



## ISO Standards Handbook: Paints and varnishes

Volume 1: General test methods

1994, Ed. 2, 486 p., ISBN 92-67-10199-4

### Contents

ISO 1512:1991	Paints and varnishes – Sampling of products in liquid or paste form
ISO 1513:1992 <sup>1)</sup>	Paints and varnishes – Examination and preparation of samples for testing
ISO 1514:1993	Paints and varnishes – Standard panels for testing
ISO 1516:1981	Paints, varnishes, petroleum and related products – Flash/no flash test – Closed cup equilibrium method
ISO 1517:1973	Paints and varnishes – Surface-drying test – Ballotini method
ISO 1518:1992	Paints and varnishes – Scratch test
ISO 1519:1973	Paints and varnishes – Bend test (cylindrical mandrel)
ISO 1520:1973	Paints and varnishes – Cupping test
ISO 1522:1973	Paints and varnishes – Pendulum damping test
ISO 1523:1983	Paints, varnishes, petroleum and related products – Determination of flashpoint – Closed cup equilibrium method
ISO 1524:1983	Paints and varnishes – Determination of fineness of grind
ISO 2409:1992	Paints and varnishes – Cross-cut test
ISO 2431:1993 <sup>2)</sup>	Paints and varnishes – Determination of flow time by use of flow cups
ISO 2808:1991	Paints and varnishes – Determination of film thickness
ISO 2809:1976	Paints and varnishes – Determination of light fastness of paints for interior use
ISO 2810:1974	Paints and varnishes – Notes for guidance on the conduct of natural weathering tests
ISO 2811:1974	Paints and varnishes – Determination of density
ISO 2812-1:1993	Paints and varnishes – Determination of resistance to liquids – Part 1 General methods
ISO 2812-2:1993	Paints and varnishes – Determination of resistance to liquids – Part 2: Water immersion method
ISO 2813:1978	Paints and varnishes – Measurement of specular gloss of non-metallic paint films at 20 degrees, 60 degrees and 85 degrees

<sup>1)</sup> Includes ISO 1513:1992/Cor.1:1994

<sup>2)</sup> Includes ISO 2431:1993/Cor.1:1994

<b>ISO 2814:1973</b>	Paints and varnishes – Comparison of contrast ratio (hiding power) of paints of the same type and colour
<b>ISO 2815:1973</b>	Paints and varnishes – Buchholz indentation test
<b>ISO 2884:1974</b>	Paints and varnishes – Determination of viscosity at a high rate of shear
<b>ISO/TR 3172:1974</b>	Paints and varnishes – Large scale brushing test
<b>ISO 3231:1993</b>	Paints and varnishes – Determination of resistance to humid atmospheres containing sulfur dioxide
<b>ISO 3232:1974</b>	Paints and varnishes – Determination of quantity of material in a container
<b>ISO 3233:1984</b>	Paints and varnishes – Determination of volume of dry coating (non-volatile matter) obtained from a given volume of liquid coating
<b>ISO 3248:1975</b>	Paints and varnishes – Determination of the effect of heat
<b>ISO 3251:1993</b>	Paints and varnishes – Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes
<b>ISO 3270:1984</b>	Paints and varnishes and their raw materials – Temperatures and humidities for conditioning and testing
<b>ISO 3668:1976</b>	Paints and varnishes – Visual comparison of the colour of paints
<b>ISO 3678:1976</b>	Paints and varnishes – Print-free test
<b>ISO 3679:1983</b>	Paints, varnishes, petroleum and related products – Determination of flashpoint – Rapid equilibrium method
<b>ISO 3680:1983</b>	Paints, varnishes, petroleum and related products – Flash/no flash test – Rapid equilibrium method
<b>ISO 3856-1:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 1: Determination of lead content – Flame atomic absorption spectrometric method and dithizone spectrophotometric method
<b>ISO 3856-2:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 2: Determination of antimony content – Flame atomic absorption spectrometric method and Rhodamine B spectrophotometric method
<b>ISO 3856-3:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 3: Determination of barium content – Flame atomic emission spectrometric method
<b>ISO 3856-4:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 4: Determination of cadmium content – Flame atomic absorption spectrometric method and polarographic method
<b>ISO 3856-5:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 5: Determination of hexavalent chromium content of the pigment portion of the liquid paint or the paint in powder form – Diphenylcarbazine spectrophotometric method
<b>ISO 3856-6:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 6: Determination of total chromium content of the liquid portion of the paint – Flame atomic absorption spectrometric method

<b>ISO 3856-7:1984</b>	Paints and varnishes – Determination of "soluble" metal content – Part 7: Determination of mercury content of the pigment portion of the paint and of the liquid portion of water-dilutable paints – Flameless atomic absorption spectrometric method
<b>ISO 3905:1980 <sup>3)</sup></b>	Paints and varnishes – Determination of contrast ratio (opacity) of light coloured paints at a fixed spreading rate (using black and white charts)
<b>ISO 3906:1980 <sup>4)</sup></b>	Paints and varnishes – Determination of contrast ratio (opacity) of light coloured paints at a fixed spreading rate (using polyester film)
<b>ISO 4617-1:1978</b>	Paints and varnishes – List of equivalent terms – Part 1: General terms
<b>ISO 4617-2:1982</b>	Paints and varnishes – List of equivalent terms – Part 2
<b>ISO 4617-3:1986</b>	Paints and varnishes – List of equivalent terms – Part 3
<b>ISO 4617-4:1986</b>	Paints and varnishes – List of equivalent terms – Part 4
<b>ISO 4618-1:1984</b>	Paints and varnishes – Vocabulary – Part 1: General terms
<b>ISO 4618-2:1984</b>	Paints and varnishes – Vocabulary – Part 2: Terminology relating to initial defects and to undesirable changes in films during ageing
<b>ISO 4622:1992</b>	Paints and varnishes – Pressure test for stackability
<b>ISO 4623:1984</b>	Paints and varnishes – Filiform corrosion test on steel
<b>ISO 4624:1978</b>	Paints and varnishes – Pull-off test for adhesion
<b>ISO 4627:1981</b>	Paints and varnishes – Evaluation of the compatibility of a product with a surface to be painted – Methods of test
<b>ISO 4628-1:1982</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 1: General principles and rating schemes
<b>ISO 4628-2:1982</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 2: Designation of degree of blistering
<b>ISO 4628-3:1982</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 3: Designation of degree of rusting
<b>ISO 4628-4:1982</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 4: Designation of degree of cracking
<b>ISO 4628-5:1982</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 5: Designation of degree of flaking
<b>ISO 4628-6:1990</b>	Paints and varnishes – Evaluation of degradation of paint coatings – Designation of intensity, quantity and size of common types of defect – Part 6: Rating of degree of chalking by tape method
<b>ISO 6270:1980</b>	Paints and varnishes – Determination of resistance to humidity (continuous condensation)
<b>ISO 6272:1993</b>	Paints and varnishes – Falling-weight test

<sup>3)</sup> Includes ISO 3905:1980/Amendment 1:1981

<sup>4)</sup> Includes ISO 3906:1980/Amendment 1:1981

<b>ISO 6441:1984</b>	Paints and varnishes – Indentation test (spherical or pyramidal)
<b>ISO 6503:1984</b>	Paints and varnishes – Determination of total lead – Flame atomic absorption spectrometric method
<b>ISO 6504-1:1983</b>	Paints and varnishes – Determination of hiding power – Part 1: Kubelka-Munk method for white and light-coloured paints
<b>ISO 6713:1984</b>	Paints and varnishes – Preparation of acid extracts from paints in liquid or powder form
<b>ISO 6860:1984</b>	Paints and varnishes – Bend test (conical mandrel)
<b>ISO 7252:1984</b>	Paints and varnishes – Determination of total mercury – Flameless atomic absorption spectrometric method
<b>ISO 7253:1984</b>	Paints and varnishes – Determination of resistance to neutral salt spray
<b>ISO 7254:1984</b>	Paints and varnishes – Assessment of natural spreading rate – Brush application
<b>ISO 7724-1:1984</b>	Paints and varnishes – Colorimetry – Part 1: Principles
<b>ISO 7724-2:1984</b>	Paints and varnishes – Colorimetry – Part 2: Colour measurement
<b>ISO 7724-3:1984</b>	Paints and varnishes – Colorimetry – Part 3: Calculation of colour differences
<b>ISO 7877:1984</b>	Paints and varnishes – Coating of test panels at a specified spreading rate – Brush application
<b>ISO 8130-1:1992</b>	Coating powders – Part 1: Determination of particle size distribution by sieving
<b>ISO 8130-2:1992</b>	Coating powders – Part 2: Determination of density by gas comparison pycnometer (referee method)
<b>ISO 8130-3:1992</b>	Coating powders – Part 3: Determination of density by liquid displacement pycnometer
<b>ISO 8130-4:1992 <sup>5)</sup></b>	Coating powders – Part 4: Calculation of lower explosion limit
<b>ISO 8130-5:1992</b>	Coating powders – Part 5: Determination of flow properties of a powder/air mixture
<b>ISO 8130-6:1992</b>	Coating powders – Part 6: Determination of gel time of thermosetting coating powders at a given temperature
<b>ISO 8130-7:1992</b>	Coating powders – Part 7: Determination of loss of mass on stoving
<b>ISO 8130-9:1992</b>	Coating powders – Part 9: Sampling
<b>ISO/TR 9038:1991</b>	Paints and varnishes – Determination of the ability of liquid paints to sustain combustion
<b>ISO 9117:1990</b>	Paints and varnishes – Determination of through-dry state and through-dry time – Method of test
<b>ISO 9514:1992</b>	Paints and varnishes – Determination of the pot-life of liquid systems – Preparation and conditioning of samples and guidelines for testing

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<sup>5)</sup> Includes ISO 8130-4:1992/Cor 1:1993

# PERFLUOROARYL SUBSTITUTED INORGANIC-ORGANIC HYBRID MATERIALS

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## ABSTRACT

A new class of perfluoroaryl substituted inorganic-organic copolymers (ORMOCER's) for integrated optics have been synthesized via hydrolysis and condensation (sol-gel processing) of novel perfluoroaryloxy-silanes followed by organic crosslinking reactions. Curing leads to transparent coatings with low NIR optical loss factors. Patterned layers for optical interconnection were fabricated by photolithographic procedures.

## INTRODUCTION

For optical applications two types of materials have gained importance: glasses and optical transparent polymers. Although inorganic glasses remain unsurpassed as optical transmission media, they are not universally suitable for the fabrication of optoelectronic devices due to their low flexibility, high brittleness and weight [1]. Polymer based optical materials like PMMA or polystyrene (PS) also have several significant disadvantages such as low heat-resistance (PMMA 80°C, PS 70°C) and relatively poor adhesion between both components and the substrate material. Several applications in optical data communication and processing demand optical materials with high flexibility, heat-resistance and low processing temperatures.

A solution for these contrasting problems may be provided by silicate-based inorganic-organic copolymers (ORMOCERs) [2]. In contrast to the well known silicones, ORMOCERs allow better tailoring towards the intended purpose of the materials and the demands of the application technology due to their flexible design [2].

ORMOCERs are hybrid inorganic-organic materials [3] composed of inorganic oxidic structures cross-linked or substituted by organic groups. They are prepared from organosilane precursors by sol-gel-processing [4] in combination with organic crosslinking of polymerizable organic functions. As a result of these functionalities the properties of the ORMOCERs can be adjusted to particular applications [2,5]. Systematic variation of composition combined with adaption to micro system technology allows great flexibility in processing. In addition to the properties resulting from the network, special functional organic groups (network-modifiers) effect additional material properties.

For applications where ORMOCERs are to be employed as optical wave guides (buffer, core or cladding) within specific data communication devices such as optical switches, distributors and amplifiers it is necessary to develop materials with a minimum of light transmission loss in the NIR-region (1300-1550 nm), where high output power optical sources like laser diodes are available. Considering the fact that CH vibrational absorption is a major loss factor in this region [1], this entails minimizing the number of carbon-hydrogen bonds per cubic centimeter. One possibility to achieve this goal is to replace the carbon-hydrogen bonds by carbon-fluorine bonds, a practice employed in conventional polymer optical materials [1]. The most efficient method with regards to the present study is to use fluorinated organosilane

<sup>\*</sup> registered trademark of Fraunhofer-Gesellschaft in Germany

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precursors in the initial step of the ORMOCER-synthesis. All commercially available fluorinated silanes to date are long-chained polyfluorinated alkylsilanes which are unsuitable in the ORMOCER-synthesis because of their very low polarity. Moreover, the low refractive index of polyfluoroalkyl-derivatives presents a problem as the majority of applications require an index greater than 1.45. However, perfluoroarylsilanes are expected to have appropriate refractive indices. In this paper the preparation of novel fluorinated alkoxy-silanes and the results concerning the optical loss of fluorinated ORMOCERs based on these silanes are described.

## GENERAL ASPECTS

A structural scheme of the novel perfluoroaryl silane type is shown in Fig. 1. The alkoxy groups allow the formation of an inorganic Si-O-Si-network by hydrolysis and condensation reactions. The attached perfluoroaryl group provides the means by which network modification or thermally or photochemically induced polymerization to build up an additional organic network may be achieved, depending on the functional group in para position of the phenyl ring.

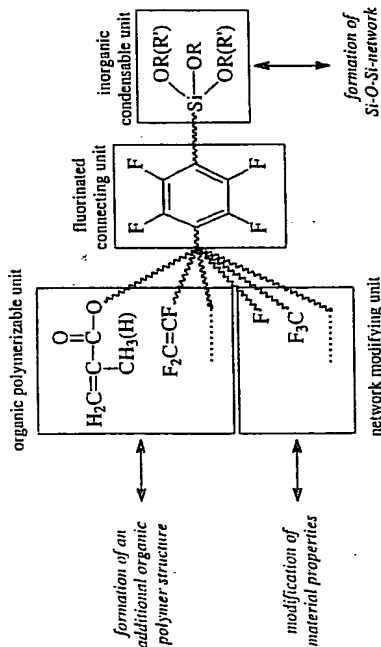


Fig. 1. General formula of the novel perfluoroaryl silanes

## EXPERIMENTAL

$^1\text{H}$ -,  $^{19}\text{F}$ - and  $^{13}\text{C}$ -NMR spectra were obtained in  $\text{CDCl}_3$  as solvent and internal standard using a Bruker WM 400 spectrometer. Vibrational spectra were recorded using a FTIR-pectrometer (Bio-Rad FTS-25) and an UV-VIS-NIR-spectrometer (Shimadzu UV 3100).

Synthesis of the fluorinated precursors was carried out by modification of a method developed by Wittingham and Jarvie [6]:

24.7 g (100 mmol) pentafluorobromobenzene, 2.65 g (110 mmol) magnesium turnings, 1.7 g (200 mmol) freshly distilled tetraethoxysilane and a few crystals of iodine were mixed together at room temperature and diethyl ether added dropwise to the vigorously stirred mixture until an exothermic reaction was observed (approx. 30 ml). After stirring and refluxing for 16 h the mixture was cooled to room temperature. An excess of n-heptane was added to precipitate the magnesium salts. Filtration gave a clear pale yellow solution. Solvents were removed and

the residue fractionally distilled under reduced pressure to yield 11.6 g (35 %) pentafluoro-phenyltriethoxysilane, b.p.  $67\text{--}70^\circ\text{C}/0.2\text{ mbar}$  and 4.5 g (20%) bis(pentafluorophenyl)diethoxysilane, b.p.  $99\text{--}101^\circ\text{C}/0.2\text{ mbar}$ .

3.92 g (10 mmol) p-bromoperfluorostyrene [8], 0.53 g (22 mmol) magnesium turnings, 8.33 g (40 mmol) freshly distilled tetraethoxysilane, 1.87 g (10 mmol) 1,2-Dibromoethane and 10 ml diethyl ether were mixed together and brought to reflux conditions until an exothermic reaction was observed (approx. 15 min). The stirring mixture maintained under those conditions for 16 h and subsequently cooled to room temperature. An excess of n-heptane was added to precipitate the magnesium salts. Filtration gave a clear pale yellow solution. Solvents were removed and the residue fractionally distilled under reduced pressure to yield 11.6 g (40 %) p-triethoxysilyl-perfluorostyrene, b.p.  $74\text{--}75^\circ\text{C}/0.2\text{ mbar}$ .

As a starting point for developing the low loss system, an established and well characterized four component system [9] was chosen with the single modification of a perfluoro-phenylsilane in exchange for the phenylalkoxy-silane constituent. The four components were  $\gamma$ -glycidyloxypropyltrimethoxysilane (GLYMO),  $\gamma$ -methacryloxypropyltrimethoxysilane (MEMO), bis(pentafluorophenyl)diethoxysilane ( $\text{P}_2\text{2}$ ) and tetraethoxysilane (TEOS). This composition was found to be suitable for thermal and/or photochemical curing in order to form the organic network.

The preparation of pentafluorophenyl substituted ORMOCER-lacquer was carried out by sol-gel processing: In the initial step the four components were mixed together without any requisite solvent; subsequent addition of the stoichiometric amount of water (1.5 mol relative to Si [7]) facilitated the construction of an inorganic network by hydrolysis/condensation reactions.

For final curing a photoinitiator (Irgacure 184, Ciba-Geigy) was added and the materials were applied onto substrates (glass or silicon wafer) by spin coating. Photo curing was carried out by UV-radiation (1000 W high pressure mercury lamp). Thermal curing took place at  $T > 120^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Precursors

The perfluoroaryl substituted alkoxy-silanes can be synthesized by a Barbier-Grignard reaction of bromoperfluoroaryl-derivatives with tetraethoxysilane. A general reaction scheme is shown in Fig. 2.

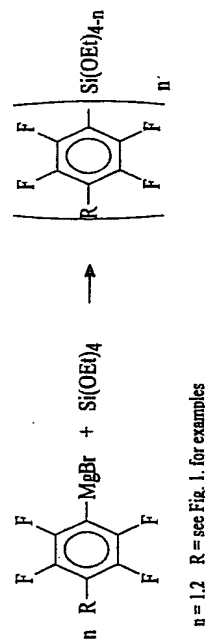


Fig. 2. Reaction scheme for the precursor synthesis

For initial studies the most convenient compounds, pentafluorophenyltriethoxysilane and bis(pentafluorophenyl)diethoxysilane, were chosen. p-Triethoxysilyl-perfluorostyrene was synthesized as a potential network-former. NMR- and IR-data are given in Table I.



Table 1. IR- and NMR-data of fluorinated silanes

<b>Pentafluorophenyltriethoxysilane</b>	
IR-data:	$\nu = 2981, 1644, 1518, 1468, 1387, 1292, 1169, 1092, 973, 792, 688 \text{ cm}^{-1}$
$^1\text{H-NMR}$ -data:	$\delta 3.94 (\text{q}, 6\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3), 1.27 (\text{t}, 9\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3)$
$^{13}\text{C-NMR}$ -data:	$\delta 149.7, 143.1, 137.6, 105.0, 59.5, 18.1$
$^{19}\text{F-NMR}$ -data:	$\delta -127.2, -151.0, -161.9$
<b>Bis(pentafluorophenyl)diethoxysilane</b>	
IR-data:	$\nu = 2983, 1644, 1519, 1469, 1387, 1293, 1167, 1094, 974, 794 \text{ cm}^{-1}$
$^1\text{H-NMR}$ -data:	$\delta 4.01 (\text{q}, 4\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3), 1.30 (\text{t}, 6\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3)$
$^{13}\text{C-NMR}$ -data:	$\delta 149.5, 143.6, 137.6, 105.8, 60.5, 17.9$
$^{19}\text{F-NMR}$ -data:	$\delta -128.1, -149.0, -161.0$
<b>P-Triethoxysilyl-perfluorooctane</b>	
IR-data:	$\nu = 2981, 1783, 1454, 1394, 1308, 1208, 1169, 1107, 1087, 986, 901, 794, 687 \text{ cm}^{-1}$
$^1\text{H-NMR}$ -data:	$\delta 3.96 (\text{q}, 6\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3), 1.28 (\text{t}, 9\text{H}, J = 7.0 \text{ Hz, OCH}_2\text{CH}_3)$
$^{13}\text{C-NMR}$ -data:	$\delta 154.1, 149.3, 144.1, 118.0, 114.3, 109.3, 59.6, 18.1$
$^{19}\text{F-NMR}$ -data:	$\delta -96.3, -111.9, -127.0, -138.1, -171.9$

#### fluorinated ORMOCERS [10]

In order to synthesize the inorganic-organic backbone, the alkoxy-silanes were hydrolyzed and polycondensed by addition of water. Water consumption and therefore the progress of the reaction step was monitored by Karl-Fischer-titration. During the course of the reaction, the ethoxy IR-absorption at  $2983 \text{ cm}^{-1}$  decreased. IR-spectroscopy also provided evidence that the sensitive Si-C-bond was not cleaved significantly under the sol-gel conditions employed. There was no decrease in intensity of the pentafluorophenyl absorption at  $1644 \text{ cm}^{-1}$ , which would be expected under conditions where bond cleavage occurs. The reactivity of the pentafluorophenyl-ethoxy-silanes within the sol gel process is insignificantly greater than that inhibited by their unfluorinated analogs, yet lower than the unfluorinated phenylmethoxy-silanes. This can be explained by the fact that the electron-withdrawing effect of the pentafluorophenyl group is rather low [11].

The obtained lacquers are homogeneous and can be used as coating materials with good wetting and adhesion properties e.g. on PMMA, glass or silicon wafer. The final organic polymerization can be induced by a photochemical or thermal process after addition of an UV-thermal initiator.

The resulting layers are transparent and optically homogeneous. The DTA trace shows endothermic events up to the range of initial decomposition ( $>200^\circ\text{C}$ ), indicating that there is no phase transition. This behaviour is consistent with a material of amorphous nature, which is also supported by X-ray diffraction analysis.

#### optical properties

The NIR spectra of a novel perfluoroaryl substituted ORMOCER-system as lacquer containing ethanol and methanol from sol gel processing, in 1 mm cuvette), resin (after evaporation of solvents, in 1 mm cuvette) and finally cured coating (thickness 1 mm) are shown in Fig. 3. As indicated earlier, a prerequisite for low optical losses in the NIR-range is a reduction of CH-bonds, which generally effects absorptions at  $1310 \text{ nm}$ , in addition to reduction of remaining SiOH- and SiOR-bonds, which are concerned with the absorption at  $1550 \text{ nm}$ . The amatic decrease in absorption intensity upon reduction of the above mentioned groups is own in Fig. 3.

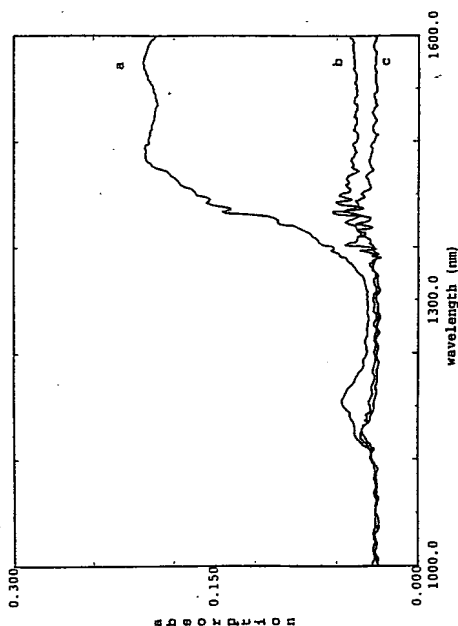


Fig.3. NIR spectra of an ORMOCER-system, containing 50 mol% P-2 as lacquer (a), resin (b) and finally cured layer (c)

In optical loss and refractive index measurements on layers and waveguides losses of  $<0.4 \text{ dB/cm}$  at  $1310 \text{ nm}$ ,  $<0.8 \text{ dB/cm}$  at  $1550 \text{ nm}$  and indices of  $>1.49$  at  $633 \text{ nm}$  were found.

#### CONCLUSIONS

Synthesis of novel perfluoroarylalkoxy-silanes has enabled the development of amorphous hybrid inorganic-organic materials with low optical loss in the NIR-range. The network exhibits better thermal stability in comparison to the majority of pure organic polymers. The material is highly adaptable and ideal for efficient device and component production, due to the possibility of either photo-initiated or thermal crosslinking.

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#### REFERENCES

- [1] T. Kaino in *Polymers for Lightwaves and Integrated Optics*, edited by L. A. Hornak (Marcel Dekker, Inc., New York, 1992), pp. 1-38.
- [2] M. Popall, J. Kappel, J. Schulz, H. Wolter in *Micro System Technologies '94*, edited by H. Reichl, A. Heuberger (VDE-Verlag, Berlin, 1994), pp. 271-280.

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# Perfluoroaryl Substituted Inorganic-Organic Hybrid Materials

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- view articles: (a) U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **7**, 2010 (1995). (b) C. nez, F. Ribot, *New J. Chem.* **18**, 1007 (1994). (c) B. M. Novak, *Adv. Mater.* **5**, 422 (1993).
- a) L. L. Hench, J. K. West, *Chem. Rev.* **90**, 33 (1990). (b) C.J. Brinker, G. Scherer, *Sol-Science*, (Academic Press, London, 1990).
- a) M. Popall, X.-M. Du, *Electrochim. Acta* **40**, 2305 (1995). (b) H. Wolter, W. Storch, H. n *Better Ceramics Through Chemistry VI*, edited by A. K. Chestham, C. J. Brinker, M. L. urney, C. Sanchez (*Mater. Res. Soc. Proc.* **346**, Pittsburgh, PA, 1994) pp. 143-149. (c) M. II, J. Kappel, M. Pilz, J. Schulz, G. Feyder, *J. Sol-Gel Sci. Technol.* **2**, 157 (1994). (d) J. , S. Amberg-Schwab, G. Schottner, *J. Sol-Gel Sci. Technol.* **2**, 189 (1994).
- .. Wittingham, A. W. Jarvie, *J. Organometal. Chem.* **13**, 125 (1968).
- . Amberg-Schwab, E. Arpac, W. Glaubitt, K. Rose, G. Schottner, U. Schubert, in *High mance Ceramic Films and Coatings*, edited by P. Vincencini (Elsevier Sci., Amsterdam, ), pp. 203-210.
- . J. Soloski, W. E. Ward, C. Tamborski, *J. Fluorine Chem.* **2**, 361 (1972/73).
- A. Popall, H. Meyer, H. Schmidt, J. Schulz, in *Better Ceramics Through Chemistry IV*, d by C. J. Brinker, D. E. Clark, D. R. Ulrich, B. J. J. Zelinsky (*Mater. Res. Soc. Proc.* **180**, urch, PA, 1990) pp. 995-1001.
- C. Roscher, M. Popall, to be published.
- W. A. Sheppard, *J. Am. Chem. Soc.* **92**, 5419 (1970).

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